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A limited comparison of ultraviolet curing and convection drying on paper permanence

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A LIMITED COMPARISON OF ULTRAVIOLET CURING AND CONVECTION DRYING ON PAPER PERMANENCE

by

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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ABSTRACT

Archivists, conservators and librarians are concerned with paper permanence. Tests have shown that paper permanence is affected by light (especially ultraviolet), temperature and humidity changes, acidity, insects and rodents, and by general use. Environmental damages are often insidious. The objective of this study is to find whether ultraviolet curing and evaporative drying as experienced in the printing industry would affect paper permanence.

Glen G. Gray's procedure for finding the reaction rate (the rate at which chemical reactions are completed) of paper is followed. This method relies on the fact that a chemical reaction occurs at speeds which depend on the molecules present and their levels of excitation. Gray compared this method to TAPPI Standard 453, concluding that the single-temperature TAPPI standard is not a reliable permanence test to compare papers with different activation energies. In Gray's multi-temperature procedure, plots of reaction rates at several temperatures are computed through the Arrhenius equation. The Arrhenius equation relates reaction rate and temperature.

The findings of this study showed a positive correlation between an increase in aging-oven temperature and a loss of folding endurance. The evaporative drying

group consistently endured fewer folds than the ultraviolet-cured group although this does not clearly indicate that heat is more damaging than ultraviolet light.

In conclusion, the evaporative drying and ultraviolet curing techniques at the levels presently used in this study were found not to be harmful to the paper tested.

CHAPTER I

INTRODUCTION

Background of the Problem

The permanence of paper can be affected by internal factors introduced during papermaking such as the kind of fibers used, the additives, and the manufacturing methods; or by external factors such as the end use of the paper and its exposure to environmental abuse. This study is concerned with paper permanence as affected by the external factor of drying methods used in printing. The life of paper may be shortened as it is contorted through the various machines and types of handling required in printing.

Although all paper does not necessarily need to be permanent, legal documents, journals and many books do require permanence. Permanence is defined as the "retention of significant end use properties...over prolonged periods."[1] A paper's resistance to folding and tearing and its retention of color and tensile strength are important measurements of its permanence. The two physical properties studied were paper acidity and folding endurance.

A property often confused with permanence is durability which is defined as: "The degree to which a paper retains its original qualities under continual usage."[2]

Durability is not a direct concern of this thesis.

Acidity

The oldest paper is believed to be approximately 2,000 years old. In contrast to this there are papers made by modern methods and materials that have deteriorated within two decades. The causes of paper deterioration were studied in the 1890s by Dr. Edwin Sutermeister who contended that decay is caused by acids introduced in the papermaking process.[3] Many researchers have confirmed Dr. Sutermeister's claims and cite acidity as a cause of fiber degradation.[4] After paper acidity induced during manufacturing was linked to paper permanence, papermakers began to offer alkaline, or acid-free papers for archival purposes. Paper acidity has also been linked to the external factor of improper storage conditions. Librarians and curators have established specifications providing acceptable environments for collections. Drying methods presently used in printing may also affect a paper's acidity or its endurance to folding.

Acidity, introduced to the paper in a variety of ways, is also a natural by-product of the aging cycle. Margaret Hey, a contributor to The Paper Conservator, discussed several causes of acidity which must be dealt with by paper conservators. One cause is the production of carboxyl groups through oxidative bleaching or from natural degradation of cellulose largely brought about by the presence of heavy metals. Acidity can arise from hydrolysis of alum, either potassium aluminum sulphate or aluminum sulphate, introduced during papermaking. Acidity can also be caused by sulphuric acid, which is activated by sulphur dioxide contacted either in the paper's environment or from irongall inks[5] which are no longer used.

Irongall writing inks were used from before the 11th century until the 19th century. They were a mixture of ferrous sulphate (copperas) with oak galls or other tannins. In a later development of irongall inks, hydrochloric or sulphuric acid was added to slow oxidation.[6] These acids applied directly to the paper caused visible damage over time.

No matter what the cause, the effect of acidity is to break down the cellulose polymer chains and cause the paper to become brittle. The actual breakdown of paper is of two types, physical and chemical.

Physical breakdown occurs either in the fibers themselves or at the point of bonding between fibers. Physical breakdown between fibers and bonding points is influenced by the pulp composition.[7] A pulp that has a high percentage of fillers would be weaker than a pulp that has a high percentage of fibers.

Chemical breakdown is caused by photochemical degradation or acid catalyzed hydrolysis. Acid catalyzed hydrolysis is the terminus of a deterioration reaction in which cellulose reacts with water under sufficient energy (heat) to produce hydrolyzed cellulose.[8] Hydrolyzed cellulose is cellulose which has been shortened by this reaction, and often leads to a loss of fiber strength.[9]

Ultraviolet (UV) light initiates a chemical type of degradation through promoting oxidation of cellulose by atmospheric oxygen. This reaction forms hydrolyzed cellulose and increases acidity. The proper wavelengths of light cause discoloration and deterioration by decomposing the rosin in rosin-sized sheets and the lignin in lignin-rich sheets.[10] UV light used to cure products is normally in the 3650 Angstrom range.

Drying Processes

Air drying, the simplest drying process, is still used to dry printing ink, but most high-speed printing processes require special drying techniques. The most common methods for drying printing ink are absorption, evaporation, oxidation and polymerization.

Absorptive drying is common to newsprint inks, and requires no drying devices. In evaporative drying, ink solvents are driven off by heated forced air. With oxidative drying, a chemical reaction within the ink causes it to dry. Polymerization occurs when a monomer reacts with a catalyst. No heat is necessary for this reaction, although it is often present.

In every case of heat, one or more types of heat transfer is in operation. There are three modes of heat transfer which differ at the molecular level: conduction, convection and radiation. In conduction, heat is transmitted from one molecule to another in a solid. Convection transfers heat through a liquid or a gas. In radiation, heat is transferred as electromagnetic wave motion.[11]

Evaporative drying uses both conduction and convection to heat the ink and to drive off the solvents forced out of the ink. The drying ovens may reach temperatures as high as 500° F.[12] Drying tunnels are designed to aid in evaporating the solvents from the ink and then to drive off the solvent-laden atomsphere with high velocity air jets. A full minute might be necessary to dry a thick coat of screen-printed ink in this way.

Polymerization by UV radiation is used in the specialty areas of metal decorating, packaging and screen printing. UV curing is best utilized when speed, gloss, abrasion resistance and nonpollution are needed or where the substrate is sensitive to heat. Although UV curing systems do often heat the substrate (because of unfiltered infrared wavelengths), the substrate remains significantly cooler than in evaporative drying. UV curing is typically in the 140° to 180° range.[13] This allows substrates which are heat-sensitive to be printed and cured without danger of dimension change.

This study attempted to relate two printing drying processes to paper permanence. The changes in pH and loss of folding endurance of paper that had been subjected to a laboratory simulation of either the evaporative drying process or of the UV curing process were compared. The term <u>injury</u> is used throughout this study to refer to the sample groups that were subjected to either of the two conditions.

Scope

The present study is not concerned with the effects of ink on the substrate, but with the effects of simulated press drying processes on paper. Ink has been shown to lessen paper permanence. Folding tests on inked areas of paper printed during the 19th century showed a reduction in flexibility as compared to uninked areas of the same sheets. Boiled linseed oil in the ink oxidized and polymerized, encrusting the paper fibers and reducing their flexibility. The results also indicated that fibers were crushed in letterpress printing.[14] A wide range of lithographic inks are dried by evaporation. Present lithographic inks are formulated with consideration to the permanence of the substrate; the inks are formulated so as to not harm the substrate over a prolonged time.[15]

A brief explanation of the paper, drying methods and tests used in this study follows. Because lignin-rich papers such as newsprint have been found to be very sensitive to UV; they were not considered. They were also disregarded because they are seldom used in high-quality printing. The paper chosen was made from a bleached chemical pulp. The fibers in it were from both hard- and softwood.

A Linde Photocure System that uses a 200 watt, medium-pressure mercury vapor lamp was used to simulate UV curing. This system was designed for screen printing. It is equipped with the option of using nitrogen gas which was not used, and carries the sheets on a belt at a constant speed. The evaporative drying method was simulated using the electrical element of an OHaus Moisture Determination Balance, a forced air blower and a mercury thermometer. Conduction and convection both occurred and a constant temperature was maintained, but the simulation was not optimal.

Paper samples were exposed to each of the two drying techniques and tested for changes in acidity and folding endurance by standard tests. The purpose of using the Arrhenius equation was to accurately predict paper permanence.

Aim of the Research

New information concerning evaporative drying and polymerization by UV was compiled. The results were compared and the Arrhenius equation was used to predict the expected lifespans of paper subjected to the two methods of drying. The effects that UV curing and evaporative drying had on paper permanence were studied.

Reasons for Interest in the Problem

Books and documents serve many levels of use. Part of their usefulness lies in the future, to provide the historical base for those not yet born to study every facet of our time. Our present culture has reaped the rewards of those who went before us, chronicling daily events, impressions and fears. Much of this information has endured on paper. Now, paper is accessible to everyone in our culture and is a common tool for expression and communication.

The present electronic age is beginning to use other methods of information storage. Magnetic tapes and cards, floppy and rigid disks are a few of the nonpermanent methods used in the paperless office. But when information must be archived it has been found that the most permanent, cheapest and easiest method to maintain is also one of the oldest--paper.[16]

The printing profession shares the responsibility of communicating the past for the future. Not only does the graphic arts industry develop methods of printing which upgrade images and are more efficient, it also develops new market products such as ink jet that link electronic media to the more accessible printed word. If drying methods cause irreversable harm to substrates, part of our history will be lost. Unfortunately, the literature available showed concern about paper permanence by librarians, conservators and papermakers, but little concern by printers.

In short, this study is concerned with the effects of two printing drying techinques on the permanence of one type of paper. The drying mechanisms used by each type, although different, could affect degradation.

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CHAPTER II

THEORETICAL BASIS

The Process of Aging

As paper degrades, its molecular chains break and rearrange. Obvious changes that take place are yellowing, increased brittleness and a loss in folding endurance. As mentioned in the Introduction, increased acidity also occurs as the hydrogen ions increase. These physical changes can be measured and are indicators of the degradation within a sheet. The measurements of an increase in pH concentration and a loss in folding endurance were used as quantifiers in the present work.

Results from the folding endurance test were used to find the rate constants of the samples. A rate constant is a proportionality constant present in some chemical reactions, that expresses a constant ratio between components in a reaction. As an independent component is used in the reaction, the dependent component is used at a steady ratio. This steady ratio is a rate constant.[1] The experiment's two independent variables--temperature and log of the rate constant--were then used in the Arrhenius equation to yield the energy required to initiate a reaction.

The Arrhenius Equation

The Arrhenius equation is concerned with the relationship between the reaction rate and temperature. It can be used to predict the lifespan of an organic material at different temperatures.

A natural rate of reaction occurs in all chemical compositons during which products are either formed or used. The rate varies depending on the components present and their equilibrium. In order to prepare the molecules for reaction, energy must be supplied. This is the activation energy. The Arrhenius equation expresses "the energy required per mole of reactants for a reaction to occur, i.e., activation energy."[2] The Arrhenius equation expresses a linear rate of change to temperature. Researchers have independently compared accelerated aging to natural aging and concluded that paper aging occurs at a constant rate.[3] This is the basis for accelerated aging studies.

The Arrhenius equation utilizes two constants as well as logarithms to calculate the activation energy.

$$A = \frac{(-2.303)\,(1.9872)\,(\log k_1/k_2)}{1/T_1 - 1/T_2}$$

In this expression:

2.303 is the conversion factor for logarithms to the base 10;

1.9872 is the universal gas constant expressed as $cal \cdot k^{-1} g^{-1} mol^{-1}$;

$\log k_1/k_2$ compares the differences between the logs of two rate constants (k_1 and k_2); and

$1/T_1 - 1/T_2$ compares the differences of the inverse of two constant temperatures.

The result of this equation is expressed in kcal/mole and is the activation energy of the material.

The rate constant measured at one time is compared to the rate constant at a later time to determine a ratio of change. This is necessary because the amount of the independent component in the compound changes as it reacts. The folding endurance results at several temperatures were used to determine the kinetic rate constants.

In following Gray's procedure when using the Arrhenius equation, two conditions must be met in order for there to be confidence in the results.

> Linear rates of change must be obtained at all temperatures used by consistent mathematical treatment of the data. This can be verified by measurements at multiple withdrawal times from accelerated-aging ovens.

Secondly,

> ...activation energy (must) be independent of temperature.[4]

It will be shown that these two criteria have been met in the present study.

Paper does not always degrade in a linear fashion. Gray outlined six operations that must be taken into consideration when predicting permanence. He writes,

> However, it is important to recognize that during degradation of paper:
> (1) Several chemical reactions can occur simultaneously.
> (2) Individual reactions can proceed at different rates.
> (3) Reactions might not proceed independently of each other.
> (4) Additional reactions may occur as the result of intermediates formed.
> (5) Rate constants can vary with temperature.
> (6) All physical properties of paper do not respond in the same fashion to chemical changes that might occur within the paper.5

The experiment was designed to quantify a change in pH and a loss in folding endurance. Both are accepted permanency tests, although neither is a final indicator of degradation. The changes in pH are shown in tables and the folding test results are analyzed in graphs. The Arrhenius equation indicates the paper's projected permanency at different temperatures.

Instrument Specifications

Standard equipment was used for the UV radiation, the aging ovens, the folding endurance test and the pH test sugments of the study. Evaporative drying was simulated using the heating element of an OHaus Moisture Determination Balance, a forced air blower and a mercury thermometer. The capabilities of all instruments were broader than was necessary for this experiment.

I. Injury of all groups. N=60

H_1, H_2, H_3, UV_1, UV_2 and UV_3

Injury of all control groups occurred later. N=10

CH_1, CH_2, CH_3, CUV_1, CUV_2 and CUV_3

II. Accelerated Aging for each oven condition. N=10

72 hour Ovens	144 hour Ovens
60° C	60° C
H1,2 and 3 UV1,2 and 3	H1,2 and 3 UV1,2 and 3
Control	Control
N=20 each Total in oven	N=10 each Total in oven
140 samples	70 samples
80° C H1,2 and 3 UV1,2 and 3	80° C H1,2 and 3 UV1,2 and3
Control	Control
N=20 each Total in oven	N=10 each Total in oven
140 samples	70 samples
105° C H1,2 and 3 UV1,2 and 3	105° C H1,2 and 3 UV1,2 and 3
Control	Control
N=20 each Total in oven	N=10 each Total in oven
140 samples	70 samples

III. Testing of all 15 groups. N=10 each.

FLOW CHART OF EXPERIMENT

CHAPTER II NOTES

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CHAPTER III

LITERATURE REVIEW

Paper manufactured from 1100 to 1500 was in direct competition with parchment. The learned manuvered politically to continue the use of the status quo. After the development of the printing press the demand for a substrate exceeded the supply of parchment. Laws in some countries allowed merchants to set up large publishing houses. Paper became the popular substrate.

Paper in its purest form is simply a mat of cellulose fibers held together by hydrogen and fiber bonding. Additives are used to enhance specific properties. By the 1600s a common practice among papermakers was to size printing and writing papers with gelatine to prevent ink feathering. In the middle of that century, alum (potassium aluminum sulphate) was introduced to assist in gelatine tub sizing.

In 1807 Moritz Friedrich Illig introduced a simplified and inexpensive method of sizing pulp in the beater. Prior to this, sizing had always been applied after the sheets were formed. Not only was the addition of alum rosin size a much easier manufacturing method, but alum could be used to "reduce foaming, enhance rattle,...improve retention of filler...and (ease) handling."[1]

In 1876 a substitute for the expensive potassium alum was developed. Aluminum sulphate was cheaper but often contained residual sulphuric acid from its manufacture.[2] Aluminum sulphate, "papermaker's alum" even now is used as a cure-all in papermaking. The advantages of aluminum sulphate in present paper manufacturing methods are in its cost, in its use in manufacturing as a precipitate for rosin size, as a mordant for dyes, and its ability to ease production. A problem encountered in today's mills is alum build-up in the plumbing system. When this occurs, sulphuric acid must be used to clean the system. To avoid this without sacrificing quality, size agents which require less alum are presently used.

Alum was targeted as a villian in the early 1900s. Dr. Edwin Sutermeister, a researcher for the S.D. Warren paper Co., showed acid to be a cause of degradation. William J. Barrow followed Sutermeister's lead and studied the relationship of paper acidity to paper permanence. In 1957 Barrow was contracted by the Council on Library Resources to find the cause of deterioration of paper manufactured in the first half of the 20th century. Through this effort he came to depend on three testing methods: a precise measurement of acidity/alkalinity, the folding endurance test and the tear resistance test.[3] Barrow stated, "the introduction of alum-rosin size contributed more to the deterioration of paper than any other development in papermaking of the 19th century, a contribution that persisted into the present century."[4]

Alum rosin size does lead to increased acidity and loss of strength in paper. Other paper manufacturing methods have also been linked to a decrease in permanence. These were outlined by W.J. Barrow in <u>Permanence/Durability of the Book: Volume V</u>[5] and are divided here into those that directly affect paper acidity and those that lead to the use of shorter, inherently weaker fibers.

Barrow directly linked the use of chlorine bleach to an increase of internal acidity.[6] In 1774 chlorine bleach was discovered by the Swedish chemist Karl Wilhelm Scheele. Chlorine is a strong oxidizing agent that unites with moisture, forming hypochlorous acid. Its use in conjunction with high temperatures which weaken fibers speeded the pulp preparation process and allowed dyed rags to be whitened and then used in papermaking. Less than fifty years after its discovery, chemistry professor John Murray and other concerned individuals were speaking out on the damages caused by improper use of chlorine bleach in papermaking.[7]

Chlorine bleaching, performed in stages, is the most often used bleaching method today. The process is much better controlled, although research is still aimed at achieving a high whiteness level without harming the pulp. In a recent article by Rudra P. Singh, good pulp quality and the ability to discontinue the use of chlorides are the advantages of a system that would bleach hardwood pulps by ozone and peroxides.[8]

In Barrow's assessment, other papermaking developments of the 1800s affected paper permanence and durability through shortening the fiber length.[9] The invention of the cotton gin in 1793 resulted in the use of cotton. Straw and wood fibers began to be used in 1800, and groundwood fibers in 1840. The Jordan refiner, developed in 1860, has been improperly used to achieve even sheet formation by chopping the wood fibers. Barrow also charged the Fourdrinier papermaking machine, invented in 1803, with decreasing the strength of the product. The paper produced is weaker not only because the machine works better with short fibers than with long fibers, but it also orients the fibers in only one direction.

Barrow found that chemically treated wood fibers were not only short, but the 19th century papers he was testing had low strength due to poor process control. The development of different chemical 'cooks' used today occurred from 1850 to 1884. The sulfite process uses a cooking solution of calcium bisulphite with an excess of sulphur dioxide.

Groundwood fibers, of which newsprint is a prime example, are notorious for their impermanence. This has been traced not only to shorter fibers, but also to retention of lignin, resins and hemicellulose in the preparation process. As aging commences, these components react chemically to form acids and break down the polymer chains. Cunha states,

> Lignin is a highly complex organic acid which surrounds and impregnates the cellulose fibers and which gives weight and substance to woody plants....Even today...(it) is not completely understood.[10]

Paper containing lignin characteristically yellows and becomes brittle upon ultraviolet exposure.

Barrow also felt that fillers added to the pulp were often a factor in the decrease of strength. The fillers took the place of fibers, added weight to the paper and weakened the bonds.[11] These factors are worth noting and serve as background to the present study.

Specifications for permanent and durable papers have been drawn up by several organizations. At least two of these include limits for acidity expressed in pH units. The pH scale of acidity to alkalinity ranges from 0 to 14, with 7 as the point of neutrality. The specifications set up by Barrow in the 1950s included a minimum of 6.5 pH and fold retention after artificial aging. In the mid-1970s The National Historical Publications and Records Commission developed a series of specifications. It called for a pH minimum of 7.5 with a 2 percent alkaline reserve and a minimum fold endurance of 30 folds at 1 kilogram of tension.[12]

The popularity of these specifications depends on the need for archival papers. Although permanence is necessary in some cases, that percent is very small. The problem is further compounded by the fact that information that does not seem important at the time of publication may become irreplaceable and of utmost importance in the future. Also the conversion by papermakers from an acid to an alkaline system is a very expensive proposition, entailing changes in chemistry and plumbing.[13]

External factors that affect paper permanence are acidity, light (especially UV), temperature and humidity changes, insects and rodents, and general use. Acid is commonly introduced by sulphur dioxide from the atmosphere. It is prevalent in cities and has been a factor since coal gas lighting was introduced in the 1800s. It is not the presence of sulphur dioxide itself that is harmful to paper, but its reaction with copper or other heavy metals in the sheet.[14] The reaction leads to sulphuric acid, one of the main causes of paper acidity cited by Margaret Hey in The Paper Conservator. Other impurities in the air that are major contributors to fiber breakdown are ammonia and ozone.[15]

The action of light on paper is not well understood but it reacts photochemically with paper ingredients other than cellulose: such as lignin, acid and resins. The reaction with these materials weakens the cellulose polymer chains bonding the paper. Ultraviolet light is the most reactive type of light.[16]

Extreme changes of temperature and humidity also drastically affect paper permanence. Much has been written concerning proper storage conditions for paper but only the ranges of temperature and humidity and the mechanism concerning paper degradation are of concern. Generally, extremes in temperature and relative humidity affect paper. Paper that has been maintained in an arid, cool condition lasts longer than paper that is subjected to change. High moisture levels coupled with heat are the worst steady conditions. These conditions are optimal for both hydrolysis of cellulose and for vermin.

Insects and rodents, as well as general use by people affect paper permanence. These usually either destroy the paper or introduce impurities. Acids, dirt and dust either spark one of the aforementioned conditions or abrade the fibers.

Cellulose polymer chains are weakened by internal and external factors. Lignin and alum rosin size are the main internal damaging factors. The most damaging external factors are acids carried in the environment, light, and changes in temperature and humidity. Heat and UV light are used to dry printing ink.

Drying Processes

The mechanisms of evaporative ink drying and UV curing systems differ at many levels. Differences are the inks, the design of the drying/curing units and the modes of heat transfer.

Inks are formulated to adapt to printing processes, environmental and economic concerns. One trend in ink formulations is toward fast solvent-release inks for the flexographic and gravure processes. The other extreme is toward high solids content inks that are adaptable to UV curable inks and coatings.[17]

Evaporative Drying

The average offset ink formula requires a drying oil, a pigment, a solvent, waxes, a drier and a plasticizer. A common web lithography ink contains solvents that have a polymeric material with pigments and additives suspended in it. This type of ink dries by first evaporating the solvent, and then precipitating the polymeric material. Problems caused by this method are pollution from the solvents emitted and substrate dimension change from excess heat.

The design of drying systems for evaporation type inks must consider both temperature levels for evaporation and polymerization of the inks and air movement of the volatile solvents. Drying hoods at each printing unit, a method commonly used in gravure printing, accelerates solvent evaporation.

Flexographic and multicolor lithographic web presses utilize a more complicated approach. These drying tunnels are designed to evaporate the solvents, soften and then solidify the resins to permit inline postpress operations. In lithography web temperature may be brought up to 300° F[18] with forced air or direct flame to vaporize the solvents. The solvents are then driven away from the web and it is cooled to about 90° F by chill rollers which set the ink. This occurs in less than one second.[19] The chilling section in web lithography is imperative for control of the surface dimension of the paper, to maintain its moisture content and to set the ink.[20]

Both the drying hood and drying tunnel designs work by heating solids in the inks, precipitating them as gases and then emitting those vapors. The modes of heat transfer in operation are conduction and convection.

Ultraviolet Curing

UV curable formulas have at least three components, but more are necessary to perform specific functions. Base polymers, cross-linking agents and photoinitiators are necessary for completion of the chemical reaction. But specific properties are enhanced by the addition of accelerators, acrylic monomers, pigments and fillers.[21]

Advantages of high solids content radiation curable formulas are that they emit less pollution than conventional inks and are not volatile. UV inks contain no solvents, only solids that react chemically to UV radiation. They form highly resistant films without pollution.

These formulas are complicated and operate in three stages. The photoinitiator in the ink is sensitive to a specific range of UV radiation, usually in the 2000 to 4000 Angstrom region.[22] The initiation begins upon irradiation and propagates as the free radicals cross-link with ingredients in the vehicle. This process is terminated when the free radicals can no longer react within the monomers. Oxygen is an excellent inhibitor of this reaction. The liquid vehicle in the UV ink is polymerized by the UV, becomes solid and is dry in 1/100th of a second.[23]

The lamp most commonly used to excite the photoinitiator in UV curable products is a 200 watt per linear inch high intensity medium pressure mercury vapor lamp. Inert nitrogen gas is often pumped into the radiated atmosphere. The nitrogen forces out oxygen which would terminate the polymerization reaction. This permits lower UV wattages to be used, saving money.[24] The curing temperatures, in the 120° to 180° F range, are much lower than conventional drying systems.[25]

Electromagnetic wave motion travels at the speed of light and can be directed. The strength of radiant heat transfer depends upon the intensity of the initial radiator, the absorption of the receptor and interactions that occur between them.[26]

Arrhenius Equation

Work by Gray, Browning and Wink, Luner and others attests to the theoretical practicality of using the Arrhenius equation to predict paper permanence.[27] Luner and Browning and Wink[28] question the variability inherent in present testing methods. Luner and Gray agree on the two conditions that must be fulfilled in order for there to be confidence in prediction results. The conditions are: the rate constants must be linear and the activation energy must be independent of temperature. Both researchers also stress that physical and chemical reactions may change the reaction rate occurring in degradation. Paper degrades at different rates depending on the pulp composition and environmental conditions.[29]

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27. Philip Luner, "Paper Permanence," TAPPI 52 (May 1969): 8Ø3.

28. B.L. Browning and W.A. Wink, "Studies on the Permanence and Durability of Paper: 1. Prediction of Paper Permanence," TAPPI 51 (April 1968): 163.

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CHAPTER IV

METHODOLOGY

The experiment consisted of three stages: injury, aging and testing. The paper was first injured using 45 seconds, 3 minutes or 15 minutes of 400°F heat or by 15 seconds, 1 minute or 3 minutes of UV radiation. The levels of injury were coded H_1, H_2, H_3, UV_1, UV_2 and UV_3 and will be referred to as such throughout this report. In the second stage the samples were placed in accelerated aging ovens for either 72 or 144 hours. Two types of ovens without humidity controls were used, forced air and gravity. The ovens were used to accelerate the rate of aging of the samples at three different temperatures, 60°C, 80°C and 105°C. The National Bureau of Standards has reported that aging paper at 100 +-2°C for 72 hours correlates to 25 years of natural aging of record papers.[1] In the third stage of the experiment the groups were subjected to the folding endurance test and to pH analysis. See flow chart at the end of Chapter II for further clarification.

Experiment

A ream of 8 1/2 X 11, 20 pound bond paper was first tested for groundwood using the phloroglucinol test. None was present. The ream was then divided into test lots of ten sheets each, in accordance with TAPPI Standard 400[2]. The sheets were cut into sample sizes, their caliper was measured according to TAPPI Standard 411[3], and a cold extraction pH test (TAPPI Useful Method 440)[4] was performed. The average of the thickness was .004", and the average pH was 4.96. See Table 1 for pH values. The acidity of the paper was probably due to alum-rosin sizing, although this was not verified.

The first phase of the experiment was then performed. Half of the sample lots were subjected to UV radiation in the Linde Photocure System without nitrogen gas. The sample times were either 15 seconds (UV_1), 1 minute (UV_2) or 3 minutes (UV_3). The samples were transported in plastic bags.

The other half of the sample lots were subjected to simulated evaporative drying. This was performed in the paper lab by using the heating element from the OHaus Moisture Determination Balance in conjunction with forced air. These samples underwent 45 seconds (H_1), 3 minutes (H_2) or 15 minutes (H_3) of the evaporative heat condition. The temperature was monitored constantly.

The control groups were injured after the rest of the injury had taken place. Paper from the original test lot that had been kept under the same conditions as the other samples was used. When studying the correlation coefficients for these lines, three were below average.

RH/ F on Day of Test	Hours in Aging Oven		Aging Oven Temps 60C	80C	105C
44%/73	0	4.96			
40%/70	0	5.80			
40%/75	72		5.05	4.95	4.85
40%/75	144		5.10	5.20	4.90

TABLE 1: Average pH reading of uninjured samples using TAPPI Useful Method 440.

After injury, the forced air oven was used to accelerate aging at 105° C. The gravity oven was set at 60° C. The samples that were to be aged at 80° C in the gravity oven were wrapped in plastic and placed in a drawer until the oven was available, then they underwent the aging phase of the experiment. The ovens were monitored each weekday. The interior temperature of each oven was measured with a mercury thermometer. After 72 hours, half of the samples were taken out, sealed in plastic and placed in the dark drawer. The other half of each oven temperature group remained in for an additional 72 hours. Then they were removed, sealed in plastic and put in the drawer with the others. The same procedure was followed for the 80° set of samples. There were no problems with this phase of the experiment.

When all the lots had been subjected to the variables of injury and aging, and had undergone a 24-hour conditioning period, they were tested. Before and after every day of testing, the ambient temperature and relative humidity were recorded. The folding endurance test was used following TAPPI Standard 511[5] in conjunction with recommendations by Cardwell.[6]

The MIT folding endurance tester is designed to double fold a sample at a 135 +-2° angle both to the right and to the left until the sample breaks. The operator may set a 0.5 to 1.5 kg tension load on the sample. A sample lot of ten from each injury level group was tested using a standard 0.5 kg dead weight to reduce variability when setting the tension spring. The folding head was checked periodically for heat build-up. All samples were tested in the cross machine direction, and with the same side orientation. Entire oven groups were tested at the same time to minimize difference in the conditions during their testing. Samples from each oven group were tested in a random fashion so as to spread out any testing equipment variability throughout each test run. The precision of the TAPPI standard method has not been determined. The testing took over a week, during which time the recorded variation in temperature range was +-3°F and in relative humidity, +-3 percent.

A cold extraction pH test was performed on the oven control groups in accordance with TAPPI Useful Method 440. One gram of the samples from each oven control group was cut into 1/4" squares, macerated in a beaker of distilled neutral pH water and allowed to sit covered one hour at room temperature. A composite evaluation of 2 pH readings to the nearest 0.1 pH unit were reported. Cold extraction methods of determining the hydrogen ion concentration of paper extracts avoid a change in pH due to heat induced during the test.

CHAPTER IV NOTES

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3. TAPPI Standard Method T-411os-76, "Thickness (Caliper) of Paper and Paperboard."
4. TAPPI Useful Method 440, "pH of Paper (Cold Extract)."
5. TAPPI Standard Method T-511su-69, "Folding Endurance of Paper (MIT Tester)."
6. R. Cardwell, L. Lyon and P. Luner, "Evaluation of a Fold Test Procedure for Paper Aging Studies," TAPPI 55 (Feb 1972): 229.

CHAPTER V

HYPOTHESES

Hypothesis I: Ultraviolet curing will not have an affect on the permanence of paper as measured by the folding endurance of paper.

Hypothesis II: Evaporative drying will not have an affect on the permanency of paper as measured by the folding endurance of paper.

CHAPTER VI

ANALYSIS AND RESULTS

Analysis

Analysis of the data was performed with a Texas Instruments TI-55 calculator using standard regression analysis formulas. The means of the loss of folding endurance per hour were computed for each lot. The means were used to plot Figures 1a-1e. Figure 1a shows a clear distinction between the three aging oven temperatures. The steepest slopes, indicating the greatest loss of folding endurance, are those of the 105° C oven, the slopes of the 80° C oven group are moderate, and the 60° C oven slopes show the least loss of folding endurance. The correlation coefficients of the regression analysis are good (see Table 2a), ranging from -.7606 to -.9832.

Mathematics were used to further quantify the findings. The logs of both the y (means of folding endurance tests) and the x (means of the aging oven times) were found. A relationship between these logs expresses the log slope of each injury group at each of the three aging temperatures. The slope of these lines defines the rate constants. See Table 3. Regression analysis of the fold endurance data for each injury level was then used to describe the best straight line for Figure 2. Data

	Time in Aging Oven @ 60° C						Log	Corr.
	0 Hrs		72 Hrs		144 Hrs		Slope	Coeff.
	y	log y	y	log y	y	log y		
H_1	15.3	1.185	9.6	.982	10.7	1.024	-2.98	-.7606
H_2	19.5	1.29	12.6	1.10	10.4	1.017	-2.72	-.9583
H_3	16.5	1.217	13.2	1.12	12.4	1.093	-3.07	-.9433
UV_1	26.8	1.428	18.1	1.26	14.5	1.161	-2.73	-.9725
UV_2	26.3	1.42	16.0	1.20	16.1	1.207	-2.83	-.8618
UV_3	22.0	1.34	16.8	1.225	15.4	1.188	-2.98	-.9832
Aging Only	21.6	1.334	17.9	1.253	16.0	1.204	-3.04	-.9832

TABLE 2a: The folding endurance means and the log of the means for each injury group at 60 C oven temperature. The log slope and correlation coefficient for each injury line is also represented.

	Time in Aging Oven @ 80° C						Log Slope	Corr. Coeff.
	0 Hrs		72 Hrs		144 Hrs			
	y	log y	y	log y	y	log y		
H_1	15.3	1.185	8.2	.914	6.8	.833	-2.61	-.9325
H_2	19.5	1.29	9.8	.99	7.1	.851	-2.52	-.9508
H_3	16.5	1.217	10.3	1.013	9.0	.954	-2.74	-.9107
UV_1	26.8	1.428	12.9	1.111	11.4	1.057	-2.59	-.9068
UV_2	26.3	1.42	13.1	1.117	12.8	1.107	-2.66	-.8756
UV_3	22.0	1.34	13.4	1.127	12.3	1.09	-2.76	-.9131
Aging Only	21.6	1.334	14.2	1.152	12.1	1.083	-2.76	-.9518

TABLE 2b: The folding endurance means and the log of the means for each injury group at 80 C oven temperature. The log slope and correlation coefficient for each injury line is also represented.

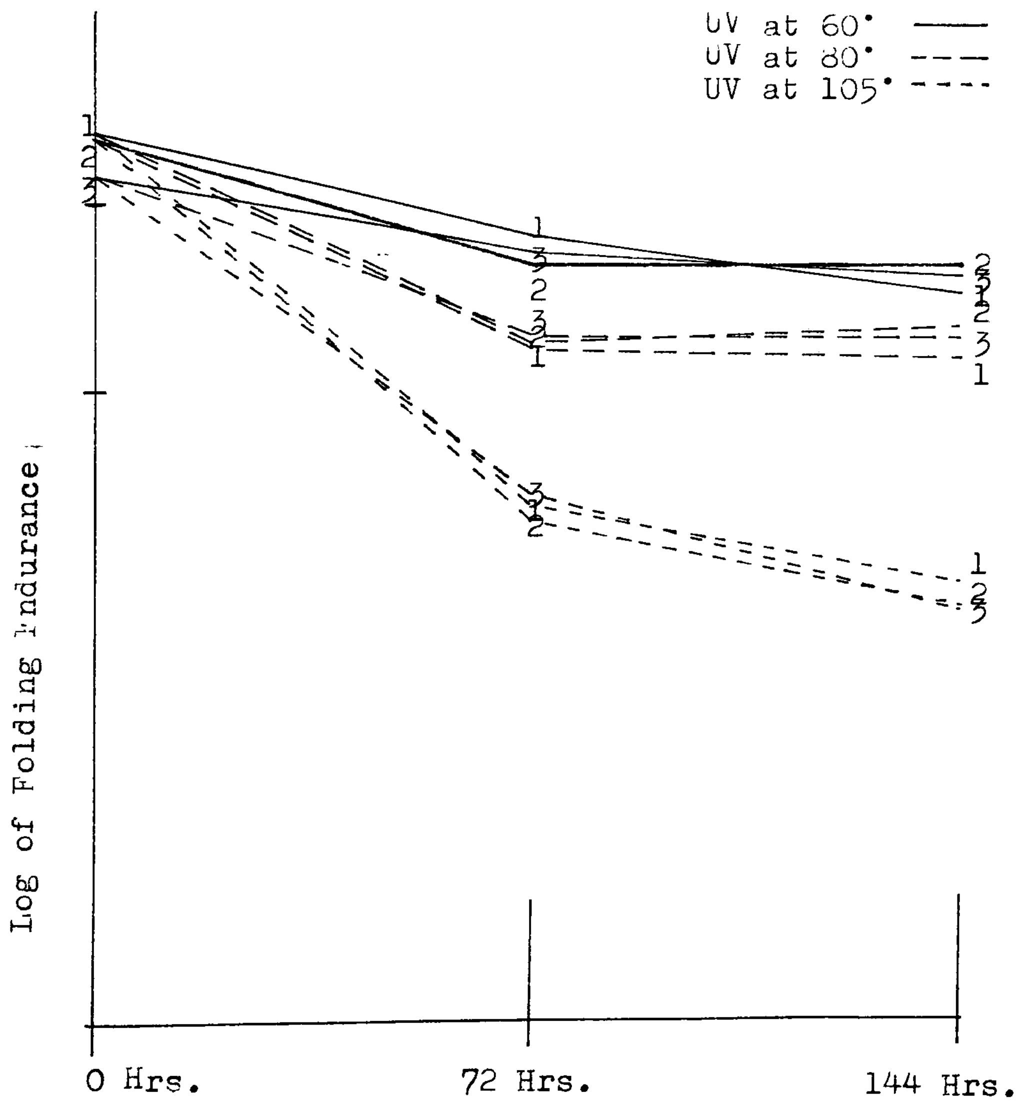
	Time in Aging Oven @ 105° C 0 Hrs		72 Hrs		144 Hrs		Log Slope	Corr. Coeff.
	y	log y	y	log y	y	log y		
H_1	15.3	1.185	4.5	.653	3.2	.505	-2.33	-.9108
H_2	19.5	1.29	6.5	.813	5.0	.699	-2.39	-.9092
H_3	16.5	1.217	5.5	.74	3.5	.544	-2.33	-.9286
UV_1	26.8	1.428	6.6	.82	5.0	.699	-2.30	-.8971
UV_2	26.3	1.42	6.3	.80	4.6	.663	-2.28	-.8991
UV_3	22.0	1.34	6.9	.839	4.5	.653	-2.32	-.9223
Aging Only	21.6	1.334	6.9	.839	4.3	.633	-2.31	-.9273

TABLE 2c: The folding endurance means and the log of the means for each injury group at 105 C oven temperature. The log slope and correlation coefficient for each injury line is also represented.

	Log Slopes 60C	80C	105C	Slope	Corr. Coeff.	Activation Energy
H_1	-2.98	-2.61	-2.33	-1799	+.9964	8.233 kcal/mol
H_2	-2.72	-2.52	-2.39	-912	+.8400	4.174 kcal/mol
H_3	-3.07	-2.74	-2.33	-2058	+.9965	9.416 kcal/mol
UV_1	-2.73	-2.59	-2.30	-1201	+.9950	5.496 kcal/mol
UV_2	-2.83	-2.66	-2.28	-1537	+.9973	7.034 kcal/mol
UV_3	-2.98	-2.76	-2.32	-1843	+.9818	8.433 kcal/mol
Control	-3.04	-2.76	-2.31	-2034	+.9944	9.310 kcal/mol

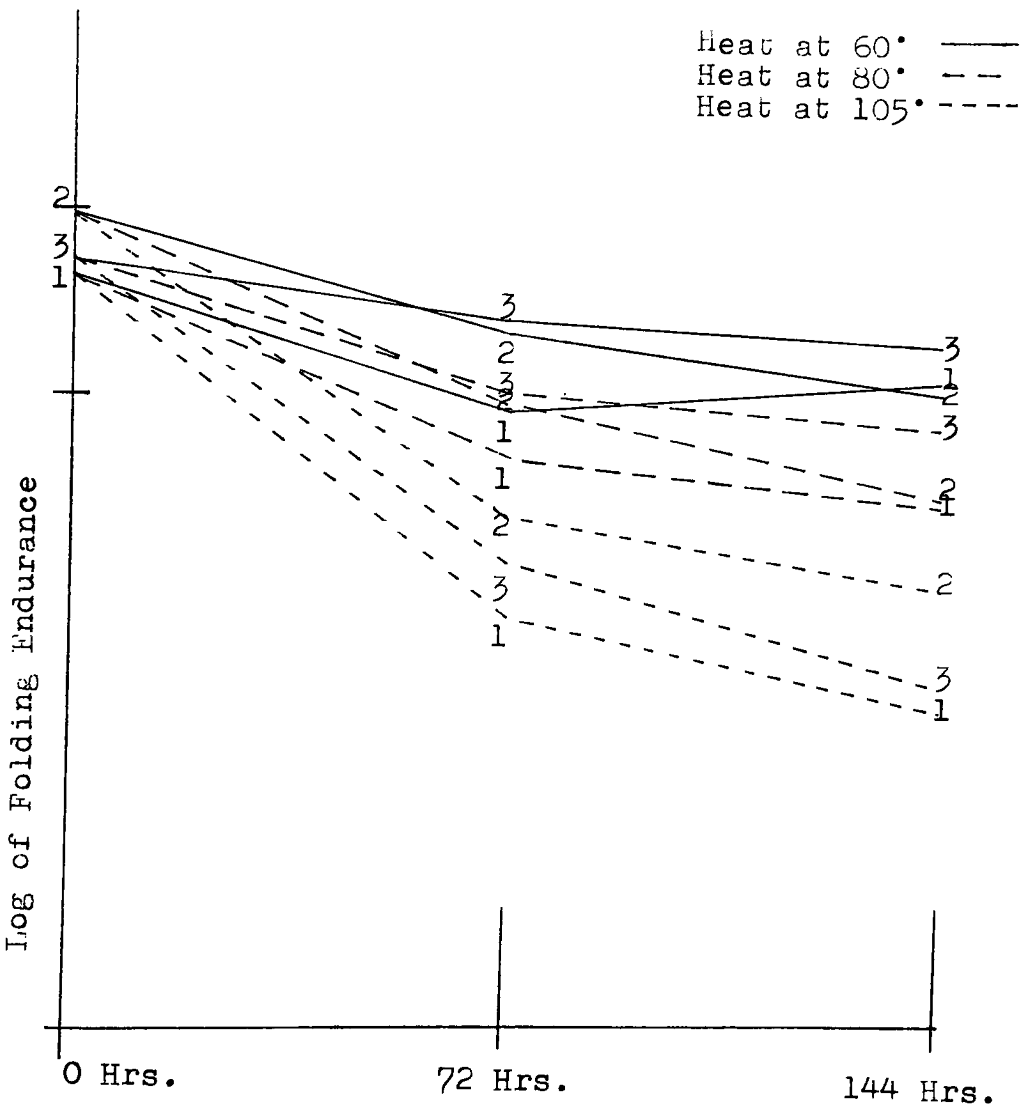
TABLE 3: The data points, regression analysis slopes from the points and the corresponding correlation coefficients for the Arrhenius graph, Figure 2. The activation energy for each injury level is also given.

Figure 1



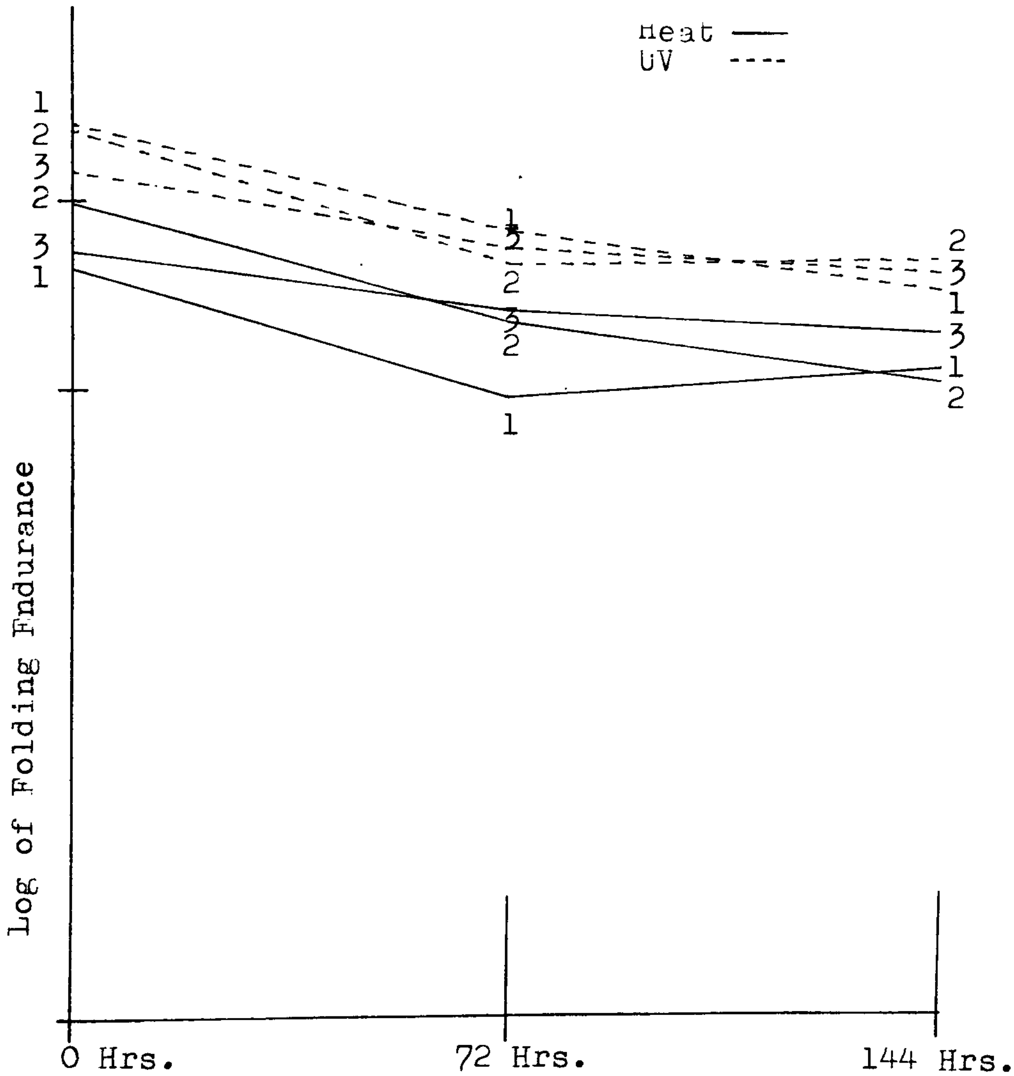
UV Injury at All Aging Oven Temperatures

Figure 1



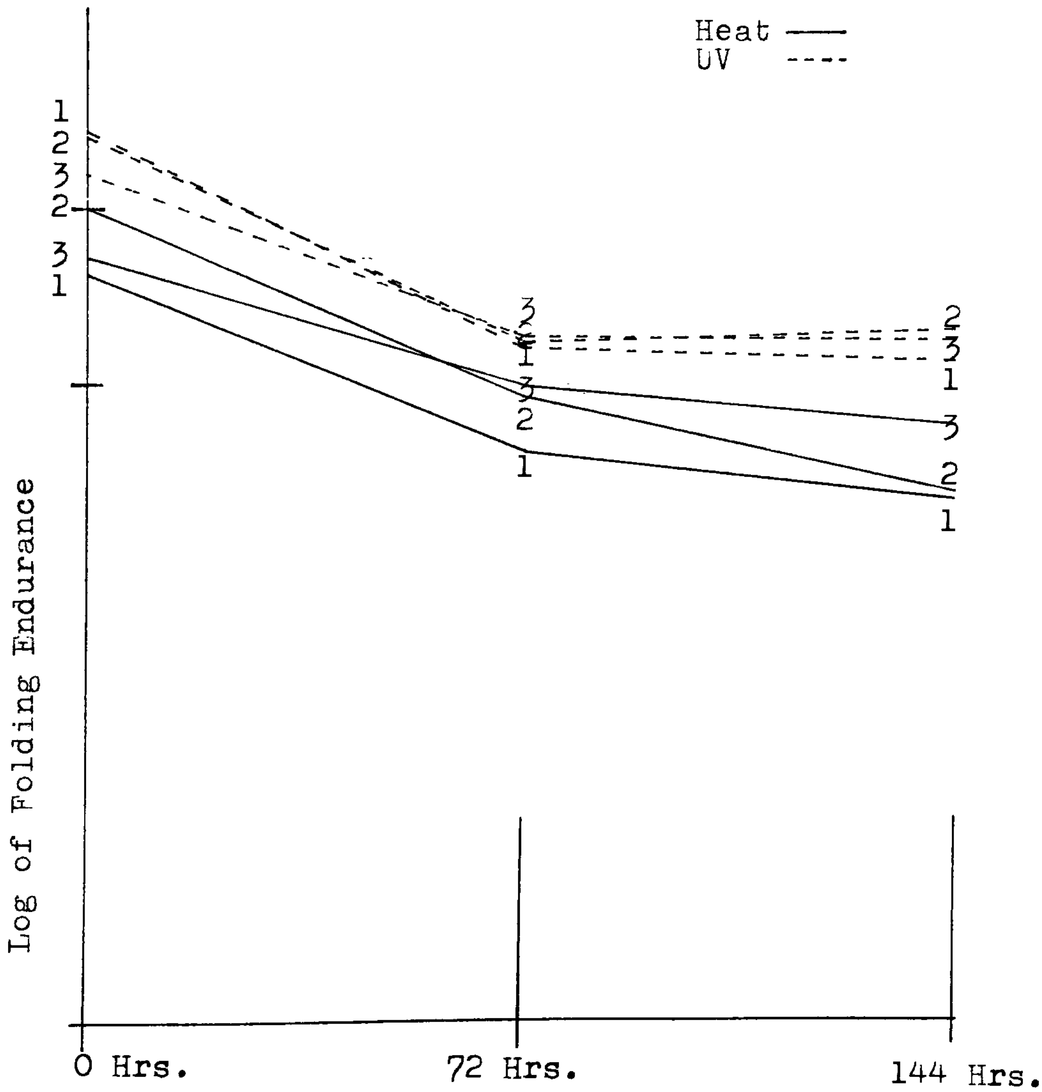
Heat Injury at All Aging Oven Temperatures

Figure 1



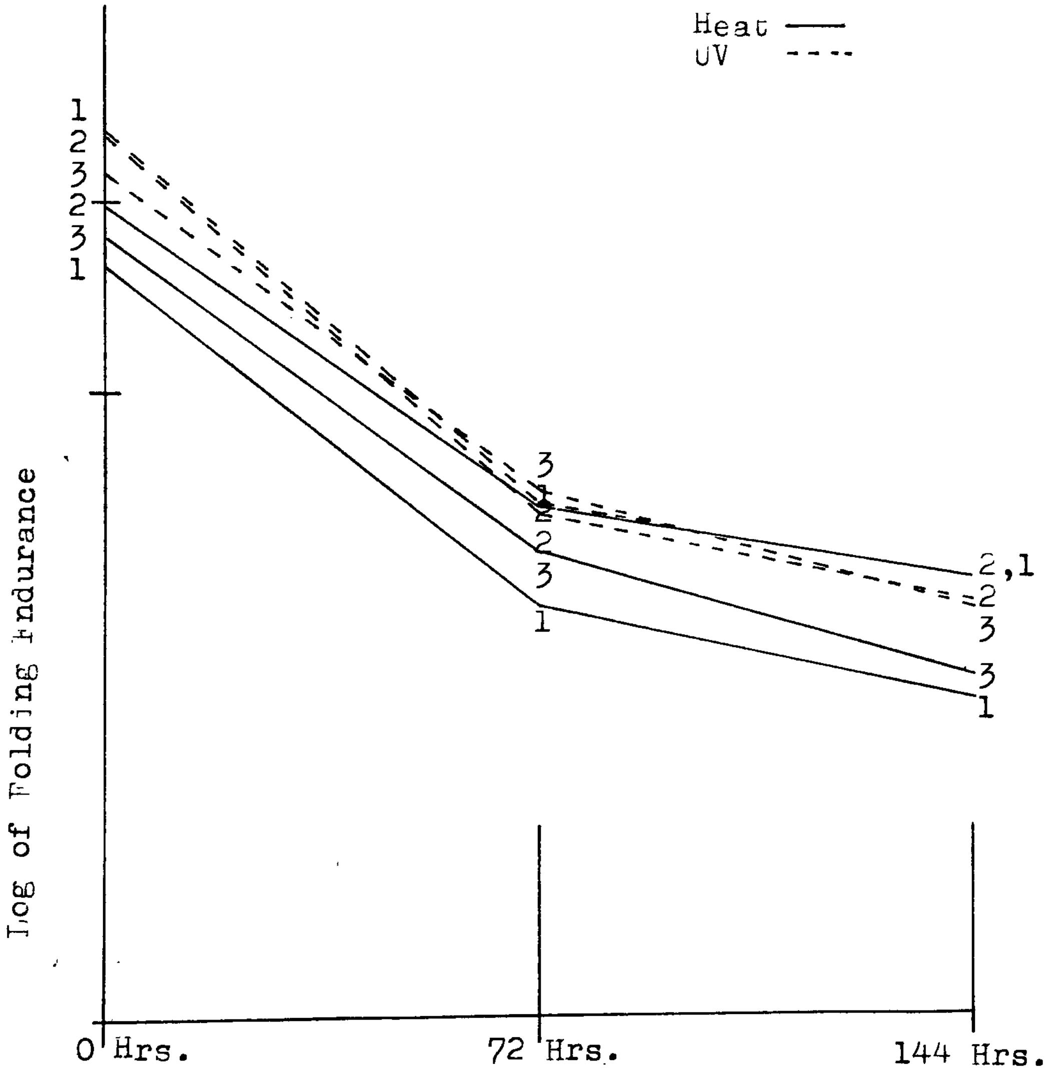
Aging at 60°C

Figure 1



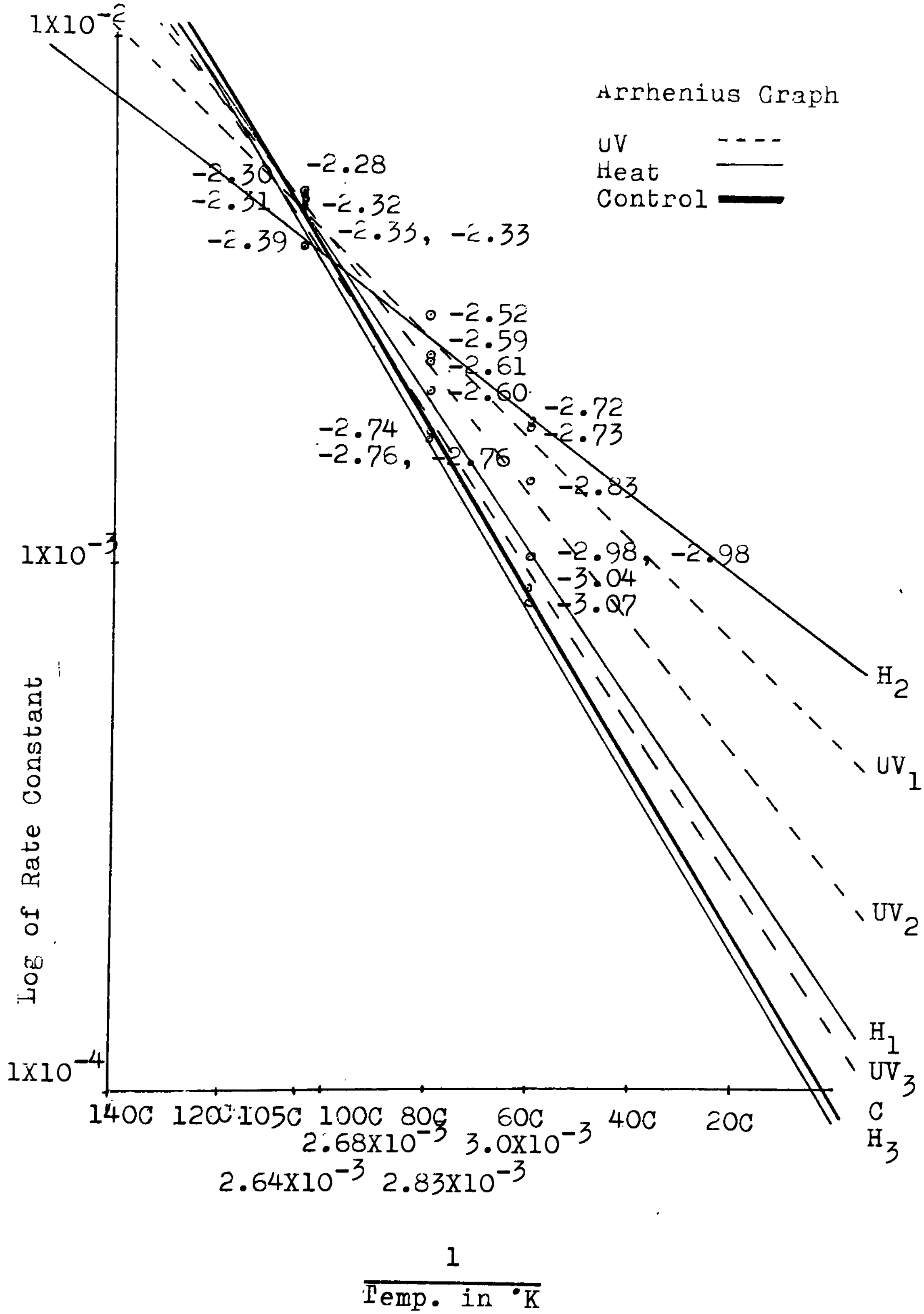
Aging at 80°C

Figure 1



Aging at 105°C

Figure 2


Arrhenius Graph
uV
Heat
Control
1X10^-2
1X10^-3
1X10^-4
Log of Rate Constant
-2.28
-2.30
-2.31
-2.32
-2.39
-2.33, -2.33
-2.52
-2.59
-2.61
-2.60
-2.72
-2.73
-2.74
-2.76, -2.76
-2.83
-2.98, -2.98
-3.04
-3.07
H2
UV1
UV2
H1
UV3
C
H3
140C 120C 105C 100C 80C 60C 40C 20C
2.68X10^-3 3.0X10^-3
2.64X10^-3 2.83X10^-3
1
Temp. in °K

yields straight line relationships when plotted in log form.

The log of the differences in rate constants (log k_1 and k_2) were applied to the Arrhenius equation, as were the differences between the inverse of the temperatures ($1/T_1$ and $1/T_2$) in degrees Kelvin. These two sets of numbers; the numerator, log k_1/k_2, and the denominator $1/T_1 - 1/T_2$, comprise the slope of the Arrhenius equation. Slopes for each injury level and their activation energies in kilocalories per mole were found using the Arrhenius equation.

The Arrhenius graph, Figure 2, plots the log rate constant against the inverse of the temperature in degrees Kelvin. The logs of the rate constants are plotted at every oven temperature used. Many of the Arrhenius lines cross each other, accounting for reversed rankings between room temperature degradation and accelerated aging degradation.

Results

Convection heat and UV curing were expected to point to a loss of folding endurance and an increase in acidity. Also, the paper that underwent longer injury times was expected to lose more fold endurance than sheets having less injury.

Neither of these effects occurred. In fact, the UV-injured paper showed exactly the opposite of the expectation. The UV_3 group resisted breakage during folding better than the UV_2 and UV_1 groups. The H_3 injury group showed little more folding endurance than the control group. See Figure 2.

One reason for the skewed heat data is probably the method of evaporation simulation. Although it was monitored carefully, some samples were visibly injured by the electrical element. The 45-second heat injury group, H_1, was especially hard to control.

Linear relationships between the logs of folding endurance and aging oven times were found for each group. See Tables 2a-2c. The correlation coefficients are lower than desired because of the consistently low folding endurance results at 72 hours.

The Arrhenius equation was solved using the regression analysis information. The equation was used to solve the activation energy in kilocalories per mole for each injury level. See Table 3. The activation energy for the control group was 9.310 kcal/mole. It was expected to be the highest because undamaged paper should need the largest amount of energy to initiate its chemical deterioration. The activation energy for the H_3 injury group, 9.416 kcal/mole, was slightly higher than the activation energy of the control group. The correlation coefficient for each was high.

The log slope for the H_3 at 60° C group was high, which could have caused the anomaly. The correlation coefficients shown in Table 3 have positive correlations. This shows that the regression analysis lines and the data points for the injury lines are closely related.

The pH results showed that the paper was acidic to start with and that as it was subjected to increasing oven temperatures, it tended to become more acidic. These tests also recorded slightly less acidity after longer aging. See Table 1. The pH results between the two sets of No Injury, No Aging groups differed by nearly a pH unit. This seems a large amount for two groups of identical paper separated by only two testing days.

A discussion of the results shown in the figures follows.

<u>Figures la-le</u>: Figures la-le plot the aging time against the log of the folding endurance. It shows that the loss of folds was more dramatic during the first 72-hour period than during the second 72-hour cycle. This result is in apparent contrast to the theory that paper degrades at a linear rate, which is a basis of this thesis. As explained in Chapter 2, many reactions occur during paper degradation. Philip Luner[1] states that a nonlinear relationship may often reflect a change in the mode of fiber//bond failure. The fact that the 72-hour folding endurance results were consistently lower at every oven temperature indicates that the paper produced the occurrence.

Figures 1a-1e also show clear separation between heat and UV injury at the two lower oven temperatures. In every case except H_1 at 105° C the heat-injured groups show more damage than the UV groups. This indicates that the amount of heat used may be more damaging than the amount of UV used. A further comparison of UV and heat is required.

An unexpected result which can be studied in Figures 1a-1e and 2 is the order of the loss of folding endurance in the UV group. At 60° C and 80° C the UV injury groups recede in endurance from UV_2 to UV_3 to UV_1. The expectation was a loss in endurance from the least injury, UV_1, to the longest radiation time, UV_3. At 105° C the UV injury level group is in the expected orientation.

The predicted relationship between aging temperature and folding endurance did occur. The fold endurance did lessen as oven temperature was increased. This is clear and acts as a double check on procedure, showing it was performed properly.

Figure 2: The Arrhenius graph, Figure 2, shows the slope of each injury level plotted as a line of inverse oven temperature against the log of rate constants. A study of Figure 2 shows the trend of a loss in folding endurance relating to injury.

The Arrhenius graph shows two groups of injury lines. One group, H_1, UV_3 the Control and H_3 lines, has longer predicted life spans while the H_2, UV_1 and UV_2

lines form a group having shorter predicted life spans at room temperature (20° C). Longer life is predicted for the higher injury levels, H_3 and UV_3. This result highlights the nonlinearity of the paper used in this study.

The Control and H_3 lines maintain parallel positions throughout the length of the graph. The H_1 and UV_3 lines each cross over the Control and H_3 lines at high temperatures, changing the ranking of the groups.

Activation energies for each of these lines are shown in Table 3. The range is from 4.174 to 9.416 kcal/mole. The Control and the H_3 lines differ by only .106 kcal/mole.

This graph shows the results of the experiment to be null. There is no clear indication that either UV or convection heat affected the permanence of the paper.

CHAPTER VI NOTES

1. Philip Luner, "Paper Permanence," TAPPI 52 (May 1969):8Ø3-Ø4.

CHAPTER VII

SUMMARY AND CONCLUSIONS

The purpose of the experiment was to study the effects of two printing drying processes on paper permanence.

The experiment had three phases; injury, aging and testing. As mentioned in Chapter VI, the problem encountered in the convection heat injury phase was in regulating the temperature without searing the samples. As this phase continued, better methods were implemented.

The control samples were injured after all the others had been tested. Consequently, the control samples had the advantage of the best methods being used to injure them.

The aging phase of the experiment consisted of placing samples from each injury level in one of three aging oven temperatures for either 72 or 144 hours. There were no problems with this phase.

The testing phase consisted of two commonly-used permanence tests: a measure of pH and a folding endurance test. Both the pH and the folding endurance tests are accepted methods of permanence testing, although neither is a conclusive test for permanence. Proponents of the use of pH tests in aging experiments conclude that pH alone is not an indicator of paper aging. Dixson and Nelson[1] report that alkalinity alone does not guarantee improved permanence. Papermaking conditions that lead to maximum bonded fiber area and tensile strength are more important permanence characteristics than paper pH.

The folding endurance test is the most sensitive single parameter of permanence, but is extremely variable. Barrow, Wink and Luner are a few who have commented on its sensitivity to temperature and humidity changes as well as the caliper and moisture content of the sheet. Cardwell published a study suggesting methods of reducing the MIT folding endurance test's variability. Several of his suggestions were incorporated in this study and are outlined in Chapter IV.

The main findings of the present study are discussed below. The type or rate of injury did not affect the paper permanence systematically, there was a clear separation between the heat-injury and the UV-injury groups at two temperatures. This can be studied in Figure 1. The heat-injured samples consistently endured fewer folds than the UV-injured samples. This observation points to the speculation that perhaps the heat and UV levels chosen were not equivalent injury levels. The injury levels used were: 45 seconds, H_1; 3 minutes, H_2; 15 minutes, H_3; 15 seconds, UV_1; 1 minute, UV_2 and 3 minutes, UV_3. The amounts of injury chosen in the present study were based on the need to achieve an effect without overstepping the possible printing range. The injury levels chosen were excessive and did not lessen the folding endurance of the paper. The results indicate that the heat injury levels were more damaging than the UV levels. But neither group ranked its loss of fold endurance according to the injury received. Two advantages of UV curing are that it is a faster and a cooler system. Both of these characteristics and the shorter injury time affected the results, showing less loss of folding endurance at nearly every level.

There was a correlation between the temperature of the aging oven and the amount of folds endured. See Figures 1c-1e. This type of relationship has often been studied and can show the linearity of paper degradation. Using this type of information, Barrow extrapolated that paper ages a time factor of 7.5 for every increase of 20°C.[2] The fact that this correlation occurred shows that the procedure was properly followed.

Three findings were inconsistent with the hypotheses: (1) the nonlinearity of the loss of fold endurance from 72 to 144 hours of aging, (2) the H_3 group had a slightly higher activation rate than the control group and (3) the UV groups showed negative correlation. These three inconsistencies are discussed below.

(1) The nonlinearity of the loss of folding endur-

ance between the 72 and the 144 hour groups indicate that synergism resulted during the procedure. As paper degrades, the molecules rearrange depending on the pulp composition and the environmental conditions. Chapter II contains an outline of six points concerning the nonlinearity of data. Four of these points from an article by Gray deal with the variation of chemical reactions during degradation. Another point states that rate constants may vary with temperature. Differences in physical breakdown may also account for nonlinearity. Luner states that aged paper breaks down by fiber failure during folding, while unaged paper may fail at the bonding points or at the fibers.[3] Both researchers stress that physical and chemical reactions may change the reaction rate. According to Browning and Wink,[4] this nonlinearism suggests that more than one first-order reaction occurred during degradation.

(2) The high activation rate of the H_3 group is most probably due to an experimental error caused by inconsistent injury of the samples.

(3) There is no explanation for the negative correlations of the UV groups.

The correlation coefficients throughout the experiment were fairly high. The correlation coefficients for the regression analysis lines compared to the data points show positive correlations throughout. This indicates that the regression analysis lines fit the original data well. See Table 3.

The prediction of paper permanence relies on paper which ages uniformly and on test results which are often variable. The paper used in the present study did not degrade uniformly. Predictions made on the permanence of the paper in this study cannot be relied upon.

The ability to predict a paper's permanence is becoming more important as a consideration in its end use. The use of the Arrhenius equation will be valuable for many of these predictions. Indications of the factors that affect a paper's permanence can be used by papermakers to produce archival sheets and by users who specify this type of product.

Recommendations for Further Research

1. Improved simulation methods.
2. Choose a paper whose degradation is linear when performing an aging study using these techniques.
3. Groundwood paper in a similar experiment.
4. Neutral pH paper in a similar experiment.
5. Absolute control of relative humidity and temperature in a similar experiment.
6. Find whether paper is a one or a multi-rate decomposition process.
7. Be assurred that the moisture loss does not affect the nonlinearity of the paper.

CHAPTER VII NOTES

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2. Frazer G. Poole, "Barrow, William James," (New York: Marcel Dekker, Inc., 1972) p. 242 in _Library Conservation: Preservation in Perspective_. eds. John P. Baker and Marguerite C. Sovoka (Stroudsburg, PA: Dowden, Hutchinson and Ross, Inc., 1978).

3. Philip Luner, "Paper Permanence." TAPPI 52 (May 1969):803-04.

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APPENDIX

A sample set of data using H_3 at 80°C.

Time in Aging Oven	Means of Folding Endurance Results at 80 C
$H_3x_1=0$	$H_3y_1=16.5$
$H_3x_2=72$	$H_3y_2=10.3$
$H_3x_3=144$	$H_3y_3= 9.0$

Formulas used in the regression analysis.

b_1 = Slope

a= Regression line intercept at y axis at x=0

y at 144= Regression line intercept at y axis at x=144

Regression Analysis of H_3 at 80° C.

H_3 y= 11.9

$$b_1 = \frac{\underline{216(10.3)} \underline{+} \underline{432(9.0)} \underline{-} \underline{216(16.5} \underline{+} \underline{10.3} \underline{+} \underline{9.0)}}{31104}$$

b= -.052

a= 15.6

144b= 7.49

y @ 144= 8.2

Formula for Log of Rate Constant:

Log of regression line intercept with y axis at x=0 minus log of regression line intercept with y axis at x=144 hours divided by Time at x=0 - Time at x=144 hours equals the Rate Constant.

Then take the log of the rate constant

H_3 at 80° C for 144 hours.

a= 15.6, log= 1.19

y at 144= 8.2, log= .91

$$\frac{1.19 - .91}{0 - 144} = \frac{.28}{144} = .0019, \text{ log} = -2.71$$

Arrhenius Equation using regression analysis data.

Formula:

$$\frac{(-2.303)(1.9872)(\log k_1/k_2}{1/T_1 - 1/T_2} = \frac{\text{kcal}}{\text{mole}}$$

H_3 @ 80° C

$$A = \frac{(2.303)(1.9872)(-2.71)}{-.32 \times 10^{-3}}$$

A= 38.757 kcal/mole

Correlation Coefficient

Formula:

H_3 at 80° C

X_i	Y_i	X_i^2	Y_i^2	X_iY_i
0	16.5	0	272.25	0
72	10.3	5184	106.09	741.6
144	9.0	20736	81.0	1296.0
216	35.8	25920	459.34	2037.6

Correlation Coefficient for H_3 line

x_i = Regression Line Points

y_i = Data Points

X_i	Y_i	X_i^2	Y_i^2	X_iY_i
16.08	16.5	258.5664	272.25	265.32
15.6	16.5	243.36	272.25	257.40
14.98	16.5	224.4004	272.25	247.17
11.98	12.4	143.5204	153.76	148.552
8.2	9.0	67.24	81.0	73.80
2.02	3.5	4.0804	12.25	7.07
68.86	74.4	941.1676	1063.76	999.312